Name: _____

Student Number: _____

Tutorial Group: _____

UNIVERSITY OF TORONTO
FACULTY OF ARTS AND SCIENCE

APRIL EXAMINATIONS 2012

CHM 138H1 S
INTRODUCTORY ORGANIC CHEMISTRY I

Duration: 3 Hours

Aids allowed: molecular models.

The examination consists of two parts, A and B, worth a total of 100 marks.

Part A consists of 15 multiple choice questions which are worth 2 marks each (total = 30 marks) and are found on pages 3–7. These questions must be answered on the computer sheet that accompanies this exam.

Part B consists of 6 short answer questions, worth a total of 70 marks, which are found on pages 7–9. These questions must be answered on the answer sheet that is attached to the back of the exam. The answer sheet may be detached.

PART A: Multiple Choice Questions.

1. THERE ARE 15 QUESTIONS ON PAGES 3–7. CHECK THAT YOU HAVE THE RIGHT NUMBER OF QUESTIONS AND PAGES.

2. Write your last name and initials in the appropriate areas of the computer form and fill in the corresponding 'bubbles' beneath them. (Hyphenated last names should be bubbled in without spaces or dashes.) Similarly, provide your student number in the box on the left of the computer form.

3. In the Subject box, write CHM 138 and your tutorial number.

4. Sign your name in the Signature box.

5. Do not make ***ANY*** marks outside of the shaded area. If any stray marks are made, the test form will not be graded.

YOUR ANSWERS ARE TO BE RECORDED ON THE COMPUTER ANSWER SHEET AND ON THIS PAPER, BOTH OF WHICH MUST BE HANDED IN AT THE END OF THE TEST. NOTHING ELSE WRITTEN ON THE TEST PAPER WILL BE MARKED.

DURING THE EXAM:

1. Clearly circle on the test paper the letter (a, b, c, d or e) for the best answer you choose for each question.

2. On the computer sheet, blacken the circle (below a, b, c, d or e) which corresponds to the answer you have chosen for each question. Make sure that only one answer is blackened. Make heavy black marks that fill the circle completely.

3. Use soft pencil only (No.2 or softer). Do not use ink or ball point pen.

4. Erase cleanly any answer you wish to change.

5. Make no stray marks on the answer sheet.

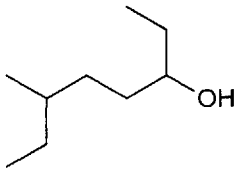
6. The computer sheet MUST be filled in DURING the time allotted for the test.

AT THE END OF THE EXAM:

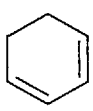
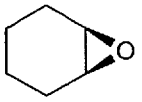
Insert your computer answer sheet into your test paper. Remain seated until all test papers have been collected.

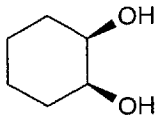
1. What is the correct IUPAC name of the compound shown at right?

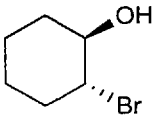
(a) 6-ethyl-3-methylhexanol
(b) 1,4-diethylpentanol
(c) 6-methyl-3-octanol
(d) 1-ethyl-4-methylhexanol
(e) 2-ethyl-5-methylheptanol

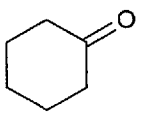


2. Determine the highest degree of unsaturation among the five structures below. How many structures have this degree of unsaturation?







(a) One structure (b) Two structures (c) Three structures
(d) Four structures (e) Five structures

3. Determine the highest oxidation level among the five structures of Question 2. How many structures have this oxidation level?

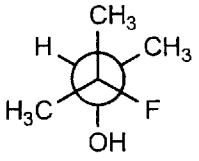
(a) One structure (b) Two structures (c) Three structures
(d) Four structures (e) Five structures

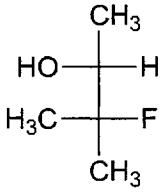
4. Which of the following statements about sp^2 hybridization is/are true?

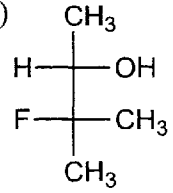
(i) All sp^2 hybridized atoms have a trigonal planar geometry.
(ii) Carbon, nitrogen and oxygen atoms may adopt sp^2 hybridization but boron atoms cannot.
(iii) All of an atom's $2s$ and $2p$ orbitals are hybridized in sp^2 hybridization

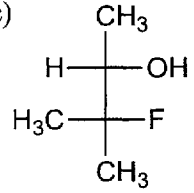
(a) only (i) is true (b) only (ii) is true (c) only (iii) is true
(d) only (i) and (ii) are true (e) only (ii) and (iii) are true.

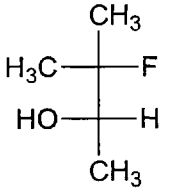
5. Which of the Fischer projections below corresponds to the following Newman projection?



(a)


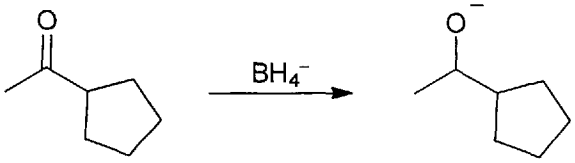
(b)


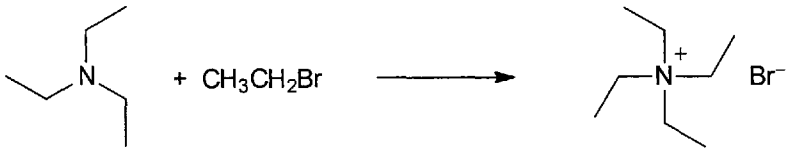
(c)


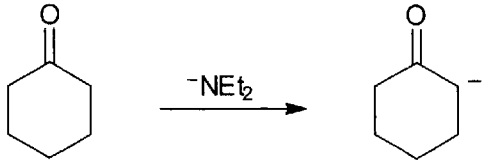
(d)


6. Which of the following transformations is a Brønsted acid-base reaction?

(a) 

(b) 

(c) 

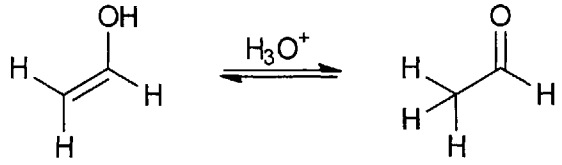
(d) 

(e) None of these is a Brønsted acid-base reaction.

7. A molecule with eight carbon atoms and three degrees of unsaturation yields two molecules of CO_2 and a compound with molecular formula $C_6H_8O_2$ upon oxidation with acidic $KMnO_4$. The starting compound must have contained:

(a) two rings (b) oxygen atoms (c) di-substituted alkenes
(d) a diol (e) a cyclobutane ring

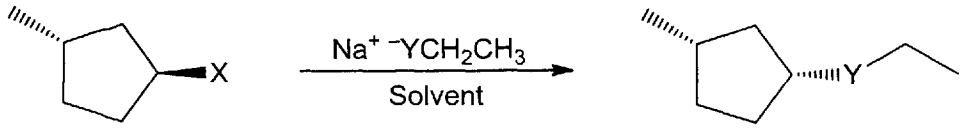
8. The acid-catalyzed isomerization reaction between vinyl alcohol and acetaldehyde has an equilibrium constant $K = 3.3 \times 10^6$. From this information, which of the following can be stated with certainty?



(i) The isomerization reaction takes place quickly.
(ii) The base-catalyzed isomerization reaction between vinyl alcohol and acetaldehyde will also have an equilibrium constant $K = 3.3 \times 10^6$.
(iii) The bond dissociation energy of a C–H bond is greater than that of an O–H bond.

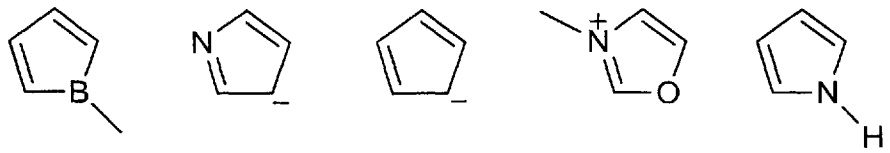
(a) Only (i) can be stated with certainty. (b) Only (ii) can be stated with certainty.
(c) Only (i) and (iii) can be stated with certainty. (d) Only (ii) and (iii) can be stated with certainty.
(e) All of i, ii and iii can be stated with certainty.

9. Which combination of starting compound X, reagent Y and solvent would lead to the highest yield of the desired product?



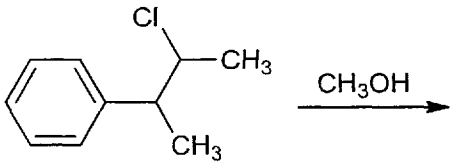
	X	Y	Solvent
(a)	OTs	O	CH_3OH
(b)	I	S	CH_3CN
(c)	Cl	S	H_2O
(d)	F	O	DMSO
(e)	I	O	DMF

10. Which of the following compounds is NOT aromatic?

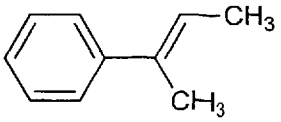


(a) (b) (c) (d) (e)

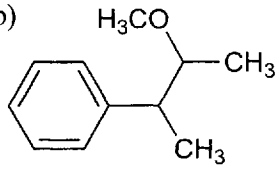
11. Which of the following products is <u>least</u> likely to form from the reaction below?



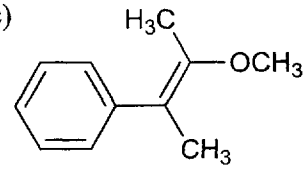
(a)



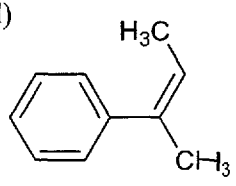
(b)



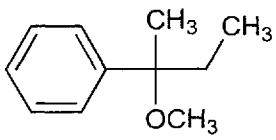
(c)



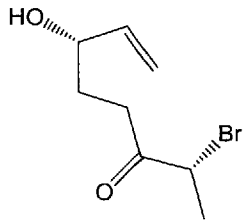
(d)



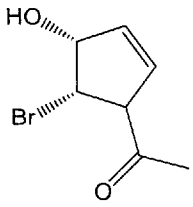
(e)



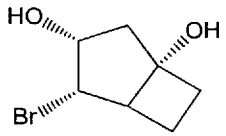
12. A compound of formula $C_7H_9BrO_2$ has a sharp IR absorbance peak at 1715 cm^{-1} and a broad IR absorbance at 3500 cm^{-1}. Upon hydrogenation over a palladium catalyst, a compound with molecular formula $C_7H_{11}BrO_2$ is produced. Which of the following is the original compound?



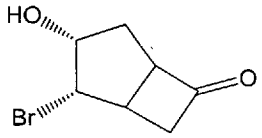
(a)



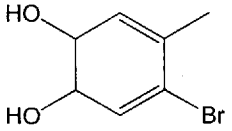
(b)



(c)



(d)

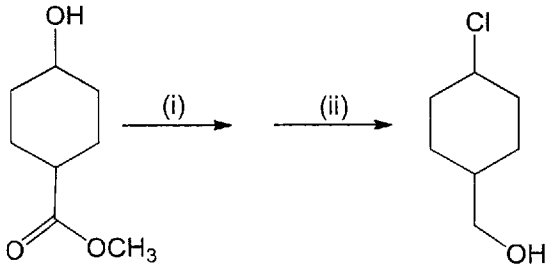


(e)

13. Which types of mechanism are generally favoured in polar aprotic solvents?

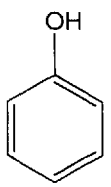
(a) Only S_N1
(b) S_N1 and S_N2
(c) E1 and E2
(d) E1 and S_N1
(e) E2 and S_N2

14. Which set of reagents could be used to efficiently achieve the transformation below.

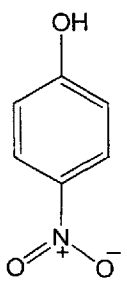


(a) (i) $LiAlH_4$, (ii) $SOCl_2$
(b) (i) $SOCl_2$, (ii) $LiAlH_4$
(c) (i) $Hg(OAc)_2$, $NaBH_4$, (ii) Cl_2
(d) (i) $NaBH_4$, (ii) TosCl
(e) (i) NaCl, (ii) H_3O^+

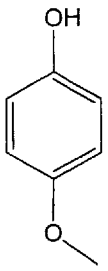
15. Rank the compounds below by decreasing pK_a values.



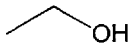
I



II



III

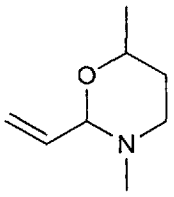


IV

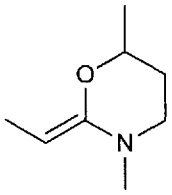
(a) **I > II > III > IV** (b) **II > I > III > IV** (c) **IV > II > III > I**
(d) **IV > III > I > II** (e) **II > IV > I > III**

PART B: Short Answer Questions.

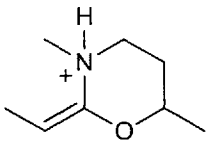
1 (*6 marks*). (a) Identify which, if any, of the structures A–E below are conjugate acid-base pairs.
(b) Identify which, if any, of the structures A–E below are conformations of the same molecule.
(c) Identify which, if any, of the structures A–E below are *E*/*Z* isomers.



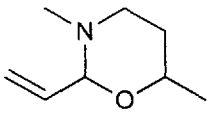
A



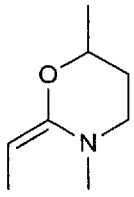
B



C



D



E

2 (*10 marks*). (a) Complete the template provided on the answer sheet to draw a chair conformation of (1*S*,2*S*)-1,2-dibromocyclohexane. **Note**: Carbon 4 has been labelled on the template.

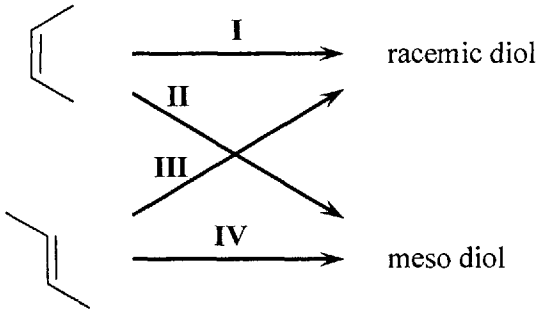
(b) Draw the chair conformation of (1*S*,2*S*)-1,2-dibromocyclohexane that arises from ring inversion (ring flipping) of the conformation in (a). Be sure to label Carbon 4 on your chair conformation.

(c) Using the table at the back of the exam, determine the energy difference between these two conformations that arises from 1,3-diaxial interactions. Show your calculation.

(d) In addition to 1,3-diaxial interactions, there is an additional source of strain present in one chair conformation that is absent in the other. Identify the origin of this additional strain.

(e) A friend of yours suggests that (1*S*,2*S*)-1,2-dibromocyclohexane could be synthesized in good yield (> 50%) from the reaction of cyclohexene with Br_2. Is your friend correct? Provide a brief explanation for your choice.

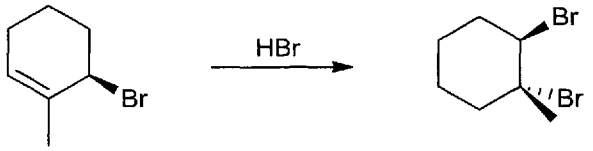
3 (*10 marks*). *Cis*- and *trans*-butene can be converted to racemic or meso diols:



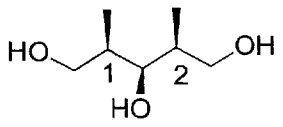
(a) Draw the **skeletal** structures of the racemic and meso diols that can form from *cis*- and *trans*-butene.

(b) Suggest appropriate reagents **I** – **IV** to bring about the above transformations. **Note**: the four reagents may not be all different. Some transformations may require more than one step.

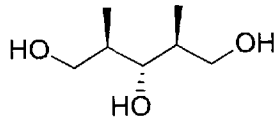
4 (*8 marks*). The following reaction yields the stereoisomer shown below as the major product. Using curved arrows to show the movement of electrons, propose a mechanism for the reaction. Do not draw the structures of transition states. Include formal charges and lone pairs of electrons where necessary.



5 (*22 marks*). A meso compound **U** with an IR absorbance at 1715 cm^{-1} is subjected to reduction with $NaBH_4$ to give a mixture of stereoisomers, **V** and **W**, both of molecular formula $C_7H_{12}O$. Oxidation of compound **V** with $KMnO_4$ and H_3O^+ gives compound **X** with molecular formula $C_7H_{10}O_5$. Treatment of compound **X** with $LiAlH_4$ gives a mixture of compounds **Y** and **Z** below.



Y



Z

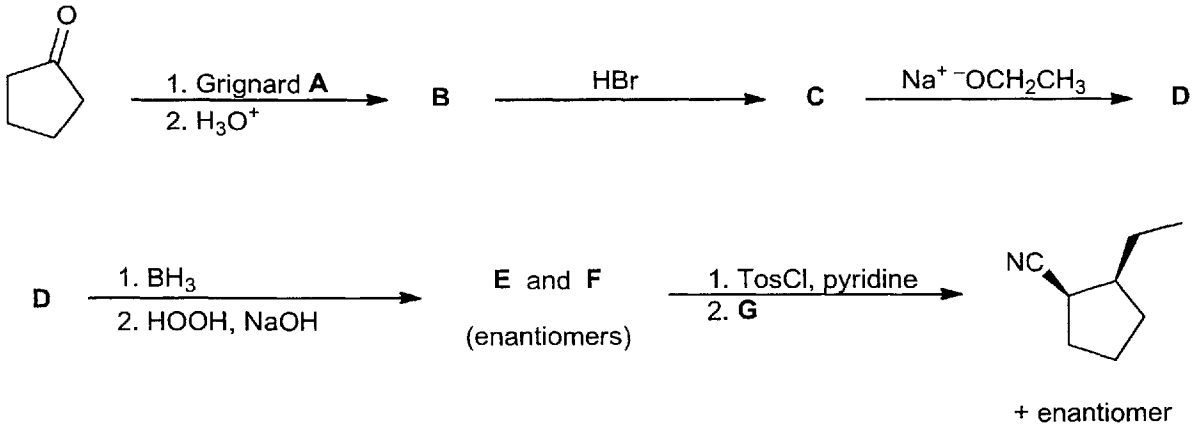
(a) In the boxes on your answer sheet, draw compounds **U**, **V**, **W** and **X**.

(b) Assign the absolute configuration (*R* or *S*) of chirality centres 1 and 2 in compound **Y**.

(c) Is the mixture of compounds **Y** and **Z** optically active? Provide an explanation for your choice.

(d) What is the term used to describe the stereochemical relationship between compounds **Y** and **Z**?

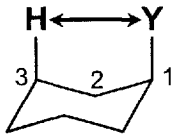
6 (*14 marks*). You wish to create the cyano-alkane at the bottom from cyclopentanone as a starting material. The synthesis will take several steps. On the answer sheet, identify the missing reagents required and the ***major*** organic products formed along the path of the synthesis.



Useful data for the CHM138 Final Examination

Steric Strain of Mono-substituted Cyclohexanes

Y	kJ/mol
-F	0.5
-Cl	1.0
-Br	1.0
-OH	2.1
$-CH_3$	3.8
$-CH_2CH_3$	4.0
$-CH(CH_3)_2$	4.6
$-C(CH_3)_3$	11.4
$-C_6H_5$	6.3
-COOH	2.9
-CN	0.4



– END OF THE EXAM –

CHM 138H1S Final Examination Answer Sheet

NAME: _____ **Student #:** _____ **Tut Gp.:** _____

Question	Mark
1	/6
2	/10
3	/10
4	/8
5	/22
6	/14
Total	/70

1 (*6 marks*).

(a)

Conjugate acid-base pair(s): _____

(b)

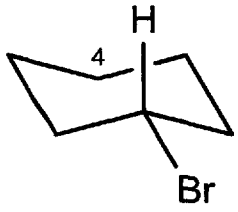
Conformations of the same molecule: _____

(c)

E/*Z* isomers: _____

2 (*10 marks*).

(a)



(b) Chair conformation from ring inversion

(c) Determine the energy difference between these two conformations that arises from 1,3-diaxial interactions. Show your calculation.

(d) The additional strain arises from _____

_____

(e) Is your friend correct? _____

_____

CHM 138H1S Final Examination Answer Sheet

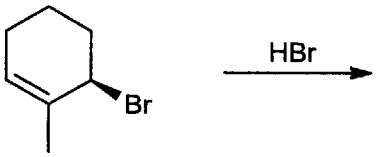
NAME: _____ **Student #:** _____ **Tut Gp.:** _____

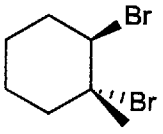
3 (*10 marks*).

(a) Racemic diol(s):		Meso diol(s):	
(b) Reagent(s) **I**	Reagent(s) **II**	Reagent(s) **III**	Reagent(s) **IV**

4 (*8 marks*).

Using curved arrows to show the movement of electrons, propose a mechanism to obtain the product shown.





CHM 138H1S Final Examination Answer Sheet

NAME: _____ **Student #:** _____ **Tut Gp.:** _____

5 (*22 marks*).

(a) Compound **U**	Compound **V**
Compound **W**	Compound **X**
(b) Absolute configuration (*R* or *S*) in **Y** Chirality centre 1 : _____ Chirality centre 2 : _____	(c) Is the mixture of compounds **Y** and **Z** optically active? (Yes/No) _____ Explanation: _____ _____ _____.
(d) What is the term used to describe the stereochemical relationship between compounds **Y** and **Z**? _____	

CHM 138H1S Final Examination Answer Sheet		
NAME: _____	**Student #:** _____	**Tut Gp.:** _____

6 (*14 marks*). *Major* organic products and reagents.

A	**B**
C	**D**
E (E and F are enantiomers)	**F** (E and F are enantiomers)
G Reagent = Solvent =	